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L5: Entry 1 of 5

File: USPT

Jan 25, 2000

DOCUMENT-IDENTIFIER: US 6017496 A

TITLE: Matrices with memories and uses thereof

DEPR:

For example, U.S. Pat. No. 4,175,183 describes a water insoluble hydroxyalkylated cross-linked regenerated cellulose and a method for its preparation. A method of preparing the product using near stoichiometric proportions of reagents is described. Use of the product directly in gel chromatography and as an intermediate in the preparation of ion exchangers is also described.

DEPR:

U.S. Pat. No. 4,178,439 describes a cationic ion exchanger and a method for preparation thereof. U.S. Pat. No. 4,180,524 describes chemical syntheses on a silica support.

DEPR:

To effect immobilization, a solution of the protein or other biomolecule is contacted with a support material such as alumina, carbon, an ion-exchange resin, cellulose, glass or a ceramic. Fluorocarbon polymers have been used as supports to which biomolecules have been attached by adsorption [see, U.S. Pat. No. 3,843,443; Published International PCT Application WO/86 03840].

DEPR:

The functionalization was performed using the readily available N-(hydroxymethyl) phthalimide, with trifluoromethanesulfonic acid as catalyst. The polystyrene grafted tubes is thoroughly washed before use to remove residual monomer, non-attached polystyrene and additives remaining from radiation grafting. The amidoalkylation proceeds smoothly in the 50% (v/v) trifluoroacetic acid--dichloromethane as solvent at room temperature for 24 hours. The predetermined loading can be obtained by changing the concentrations of reagent, catalyst and reaction time. The hydrazinolysis in refluxing ethanol gives the aminomethyl polystyrene grafted PTFE tube. The microtubes were prepared in different sizes (2-12 mm) with loading capacity range from 0.5-15 ymol per tube.

DEPR:

Functionization is performed using the readily available N-(hydroxymethyl) phthalimide, with trifluoromethanesulfonic acid [TFMSA] as a catalyst. The polystyrene grafted PTFE tube is thoroughly washed before use to remove residual monomer, non-attached polystyrene and additives remaining from radiation grafting. The amidoalkylation proceeds smoothly in the 50% (v/v) trifluoroacetic acid--dichloromethane solvent at room temperature for 24 hours. The predetermined loading can be obtained by changing the concentrations of reagent, catalyst and reaction time. The hydrazinolysis in refluxing ethanol gives the aminomethyl polystyrene grafted PTFE tube.

ORPL:

Mitchell et al., Preparation of aminomethyl-polystyrene resin by direct amidomethylation, Tetrahedron Lettrs. 42:3795-3798 (1976).

WEST



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L5: Entry 2 of 5

File: USPT

Jul 6, 1999

DOCUMENT-IDENTIFIER: US 5919971 A

TITLE: Process for the synthesis of 3-mercaptopropionic acid esters

BSPR:

Thus, J56 147,763 describes such a process by addition of H.sub.2 S to acrylic acid esters, using anion-exchange resins as catalysts, these resins having tertiary amines or quaternary ammonium hydroxides as functional groups.

BSPR:

This addition is carried out in the presence of a basic catalyst chosen from magnesium oxide and basic anion-exchange resins. These resins are chosen from those having tertiary amines or quaternary ammoniums as functional groups.

BSPR:

If an anion-exchange resin is used, the reaction pressure is generally from 3103 to 6895 kPa.

BSPR:

Preferably, when L represents a single methylene, X is a chlorine atom. In this case, a method, described by D. H. Rich and S. K. Gurwara, J. Am. Chem. Soc., 1975, 97-1575-1579, consists in reacting a chloromethylated PS-DVB resin with an excess of ammonia. Another route is based on the production of phthalimidomethylated PS-DVB resin which is converted by hydrazinolysis into a resin containing primary amine functions. The two methods for gaining access to such phthalimidomethylated resins are described in the publication by A. R. Mitchell, S. B. H. Kent, B. W. Erickson and R. B. Merrifield, Tetrahedron Letters No. 42, 1976, 3795-3798. One consists in starting with a PS-DVB resin which, on reaction with N-(chloromethyl)phthalimide, is directly converted into phthalimidomethylated resin. The other method starts with a chloromethylated PS-DVB resin which is treated with potassium phthalimide to give the corresponding phthalimidomethylated resin.

BSPR:

The method with potassium phthalimide is also applicable to resins of formula (J) in the case where L is a linear organic radical longer than the methylene radical, in particular --(CH.sub.2).sub.r--, with r being an integer greater than 1.

ORPL:

Mitchell et al., Preparation of Aminomethyl-Polystyrene Resin by Direct Amidomethylation, Tetrahedron Letters No. 42, Pergamon Press printed in Great Britain, pp. 3795-3798 (1976).

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L5: Entry 4 of 5

File: USPT

Aug 28, 1990

DOCUMENT-IDENTIFIER: US 4952608 A

TITLE: Process for preparing synthetic resins having anion exchanger properties by amidomethylating a backbone polymer containing aromatic nuclei with a specially prepared N-hydroxymethyl phthalimide.

ABPL:

The invention relates to a process for preparing anion exchangers based on crosslinked, water-insoluble organic polymers containing aromatic nuclei, in which, in the first step, N-hydroxymethylphthalimide is produced by reaction of phthalimide with aqueous formaldehyde solution in swelling agents in the presence of bases; if desired, this N-hydroxymethylphthalimide is converted in a 2nd step to the bis(phthalimidomethyl) ether or an ester of N-hydroxymethylphthalimide; said polymers are aminomethylated with N-hydroxy-methylphthalimide, bis(phthalimidomethyl) ether or an ester of N-hydroxymethylphthalimide in the presence of Friedel-Craft catalysts and swelling agents and the amidomethylated polymers are finally saponified to form the aminomethylated polymers, wherein, in the first reaction step, the base used for producing N-hydroxymethylphthalimide is sodium hydroxide solution and this sodium hydroxide solution is added in such an amount and at such a rate that the reaction of phthalimide with formaldehyde takes place in the pH range of 5 to 6.

BSPR:

The invention relates to a novel process for preparing anion exchangers based on crosslinked, water-insoluble organic polymers containing aromatic nuclei.

BSPR:

It is known to prepare anion exchangers based on crosslinked, water-insoluble organic polymers containing aromatic nuclei, for example, by amidoalkylation of said polymers in the presence of swelling agents and Friedel-Craft catalysts and subsequent hydrolysis of the amidoalkylated polymers. The proposed amidoalkylation agents were N-haloalkylimides (see U.S. Pat. No. 3,006,866), N-haloalkylimides (see U.S. Pat. No. 3,925,264), ester of N-hydroxyalkylimides (see U.S. Pat. No. 3,989,650) and bis(dicarboximidoalkyl) ethers (see U.S. Pat. Nos. 3,882,053 and 4,077,918).

BSPR:

Amidomethylating agent such as N-hydroxymethylphthalimide, the esters of N-hydroxymethylphthalimide and of bis(phthalimidomethyl) ethers were mentioned as preferred.

BSPR:

The starting product for preparing these preferred amidomethylating agents is N-hydroxymethylphthalimide. This N-hydroxymethylphthalimide is produced in the first step of the preparation of anion exchangers by reaction of phthalimide with formaldehyde in swelling agents with the addition of small amounts of zinc oxide (see U.S. Pat. No. 3,925,264, Example 1) or sodium carbonate (see U.S. Pat. Nos. 3,925,264, Example 12 and 4,077,918, Example 1).

BSPR:

For uses other than the preparation of anion exchangers, N-hydroxymethylphthalimide is conventionally prepared by reaction of phthalimide with formaldehyde in aqueous solution using sodium carbonate or sodium hydroxide as basic condensation agents (see, for example, Org. Reactions 14, page 130 and J. Org. Chem. Vol. 37 (1972), pages 391-393). Surprisingly, it has been found that anion exchangers based on crosslinked, water-insoluble organic polymers containing aromatic nuclei and having an improved total capacity and in

particular improved mechanical and osmotic stability are obtained and, in addition, the time for the preparation of the anion exchangers is substantially reduced, that is the space-time yields of the preparative processes can be substantially increased, if in the reaction of phthalimide and formaldehyde in the swelling agent sodium hydroxide solution is used as the basic condensation agent and, in addition, the reaction is carried out within a specific pH range.

BSPR:

Although it was known to use sodium hydroxide as the condensation agent in the preparation of N-hydroxymethyl phthalimide in aqueous solutions, the replacement of sodium carbonate by sodium hydroxide in the preparation of N-hydroxymethylphthalimide to be used as amidoalkylating agent for organic polymers, that is in the preparation of N-hydroxymethylphthalimide in swelling agents, was in no way obvious, since sodium carbonate and sodium hydroxide are used in the reactions of phthalimide and formaldehyde in aqueous solutions as equivalent condensation agents. Therefore, there were no grounds for assuming that the replacement of sodium carbonate solution by sodium hydroxide solution in the preparation of N-hydroxyphthalimide in swelling agents could have any advantage, in particular it was not to be expected that the use of sodium hydroxide solution in the first process step of the preparative process could lead to an improvement in the stability of the finished anion exchangers.

BSPR:

Therefore, the invention relates to a process for preparing anion exchangers based on crosslinked, water-insoluble organic polymers containing aromatic nuclei, in which, in the first step, N-hydroxymethylphthalimide is produced by reaction of phthalimide with aqueous formaldehyde solution in swelling agents in the presence of bases; if desired, this N-hydroxymethylphthalimide is converted in a second step to the bis(phthalimidomethyl) ether or an ester of N-hydroxymethylphthalimide; said polymers are amidomethylated by amidomethylation with N-hydroxymethylphthalimide, with esters of N-hydroxymethylphthalimide or with bis(phthalimidomethyl) ether in the presence of Friedel-Craft catalysts and swelling agents and the amidomethylated polymers are finally saponified to form the aminomethylated polymers, characterized in that, in the first reaction step, the base used for producing N-hydroxymethylphthalimide is sodium hydroxide solution and this sodium hydroxide solution is added in such an amount and at such a rate that in the reaction mixture a pH value is maintained in the range of 5 to 6.

BSPR:

The measure according to the invention of reacting phthalimide and formaldehyde in the pH range of 5 to 6 and adjusting and maintaining this range by adding sodium hydroxide solution brings about the following important advantages compared to the previously described processes in which zinc oxide and sodium carbonate are used as bases and in which a specific pH was neither adjusted nor maintained in the reaction solutions:

BSPR:

3. The anion exchangers are obtained in a calculable, constant and improved basicity yield (basicity yield=volume of the anion exchanger.times.total capacity of the anion exchanger; total capacity=val of amino groups/l of anion exchanger).

BSPR:

4. The anion exchangers have an improved mechanical and osmotic stability.

BSPR:

Phthalimide and 20-40% strength aqueous formaldehyde solution (molar ratio of phthalimide:formaldehyde about 1:1-1.5) are introduced into the swelling agent (amount of swelling agent: approximately 3-6 parts by weight per part by weight of phthalimide). The suspension obtained in this manner is heated to temperatures from 60.degree. to 80.degree. C. with stirring and adjusted to a pH of 5-6 by adding 20 to 50% strength aqueous sodium hydroxide solution and maintained during the reaction in this range, if necessary by addition of more sodium hydroxide solution. The pH is determined by means of an electrode immersed in the agitated suspension. The end of the reaction can be recognized by the conversion of the suspension to a cloudy solution. The stirrer is switched off to allow separation of the phases. The organic bottom layer containing the N-hydroxymethylphthalimide is separated off and dried.

BSPR:

The solution of N-hydroxymethylphthalimide in the swelling agent obtained in this manner is either used directly for the amidomethylation of the crosslinked, water-insoluble organic polymers containing aromatic nuclei or alternatively, the N-hydroxymethylphthalimide is first converted to the bis(phthalimidomethyl) ether or to an ester and the ether or the ester is used for the amidoalkylation reaction. The amidomethylation of the organic polymers using the solution of the N-hydroxymethylphthalimide, the bis(phthalimidomethyl) ether or the esters of N-hydroxymethylphthalimide in the swelling agents is carried out in a manner known per se, for example by the methods described in U.S. Pat. Nos. 3,925,264, 3,882,053, 4,077,918 and 3,989,650.

BSPR:

The amidomethylation of the organic polymers may be illustrated by means of the amidomethylation using the bis(phthalimidomethyl) ether (A) and by means of the amidomethylation using the ester of acetic acid with N-hydroxymethylphthalimide (B):

BSPR:

A. To the solution of N-hydroxymethylphthalimide in the swelling agent obtained in the first process step are added catalytic amounts of sulphuric acid (0.07 mole of H₂SO₄ per mole of N-hydroxymethylphthalimide), the solution is heated to the reflux temperature with stirring and stirred at this temperature until the ether formation is completed (the course of the ether formation is monitored by chromatography; the yield of ether is approximately quantitative). The suspension present after the completion of ether formation is cooled to about room temperature and the Friedel-Craft catalyst intended for the amidomethylation, for example iron(III) chloride, tin tetrachloride or, preferably, sulphur trioxide is added. The polymer to be amidomethylated is introduced into this mixture (amount of polymer: ratio of mole of aromatic nuclei contained in the polymer:bis(phthalimidomethyl) ether=1:0.5-4, preferably 1:0.75-2.5). The reaction mixture is heated to temperatures from 65.degree. to 80.degree. C. with stirring and then stirred at this temperature for 18 hours. After cooling to room temperature, the phthalimido methylated polymer is separated off from the liquid phase (the swelling agent), taken up in deionized water and freed of adherent swelling agent by azeotropic distillation. Finally, the phthalimidomethylated polymer is saponified in a known manner, for example by alkaline or acid hydrolysis or by reaction with hydrazine and subsequent acid hydrolysis in the presence or absence of an organic solvent; this organic solvent can be, for example, the swelling agent used for the amidomethylation.

BSPR:

B. The amidomethylation with esters of N-hydroxymethylphthalimide, for example the ester of acetic acid, is carried out by admixing the dried solution of N-hydroxymethylphthalimide in the swelling agent used which had been obtained in the first process step with the amount of acetic anhydride necessary for the esterification and heating the mixture to the reflux temperature with stirring until ester formation is complete (the course of ester formation is monitored by chromatography; the yield of ester is virtually quantitative). After esterification is complete, the solution is cooled to 20.degree. to 50.degree. C., and the organic polymer to be amidomethylated is introduced with stirring (amount of polymer: ratio of moles of aromatic nuclei in the polymer: mole of ester=1:0.5-4, preferably 1:1-2.5). The polymer is swollen in the ester solution at 50.degree. to 70.degree. C. for 0.5-2 hours. The suspension is then heated to the reflux temperature, and the proposed Friedel-Craft catalyst, preferably sulphuric acid, is added, and the suspension is subsequently stirred for 20 hours at the reflux temperature.

BSPR:

Customary polyvinyl compounds which may be mentioned are for example: divinyl ether, divinylpyridine, divinyl toluenes, divinyl naphthalenes, ethylene glycol diacrylate, divinyl xylene, divinylethylbenzene, divinyl sulphone, polyvinyl or polyallyl ethers of glycol, glycerol and pentaerythritol, divinyl ketone, divinyl sulphide, N,N'-methylenediacrylamide, N,N'-methylenedimethacrylamide, N,N'-ethylenediacrylamide, 1,2-di-(.alpha.-methylmethylenesulphonamido)ethylene, trivinylbenzene, trivinyl naphthalene, polyvinylanthracenes and trivinylcyclohexane; divinylbenzene and ethylene glycol dimethacrylate are preferred. In addition, crosslinked vinyl aromatic mixed polymers can be used in

whose preparation known additives of other vinyl compounds were used such as methacrylic and acrylic compounds. However, for the preparation of anion exchanger synthetic resins, only mixed polymers which contain the additives mentioned in an amount up to about 10% by weight, based on the total weight of the monomers are in general of interest.

BSPR:

The mechanical and osmotic stability of the amino methylated bead polymers (anion exchangers) obtained in the Examples below were determined using the following test methods:

DEPR:

a. 200.4 g of phthalimide, 135.9 g (36.4% strength by weight) of formalin solution and 890.6 g of 1,2-dichloroethane are mixed together in a flask at room temperature and heated to the reflux temperature. The pH of the mixture is then adjusted to a value of 5.5 to 6.0 by the dropwise addition of 45% strength by weight of sodium hydroxide solution and maintained in this range during the reaction (the pH of the reaction mixture is determined by means of a glass electrode immersed in the stirred mixture). After about 5 to 10 minutes, a cloudy solution is formed which immediately separates into two layers after the stirrer is switched off. The bottom layer, the solution of N-hydroxymethylphthalimide in dichloroethane, is separated off and dried.

DEPR:

In the Table following the Examples, the required time for the formation of bis(phthalimidomethyl) ether, the yields of amidomethylated bead polymer and aminomethylated bead polymer, the total capacity of the aminomethylated bead polymer, the basicity yield and the results of the stability tests are summarized.

DEPR:

In Comparative Example .gamma., even after 1 hour still no clear organic phase had separated. As a large portion of the bead polymers had been broken as soon as the amidomethylation was at an end, the saponification was omitted and the mixture was discarded.

DEPR:

a. The reaction was carried out as described in Example 1 except that 114.9 g of polymer B (particle size: 0.3-0.8 mm) were now used instead of polymer A used in Example 1. Yield of amidomethylated polymer: 690 ml. The 690 ml of amidomethylated bead polymer were saponified with 1380 ml of 27% strength by weight of sodium hydroxide solution. Yield 533 ml.

DEPR:

In the Table following the Examples, the yields of amidomethylated and aminomethylated bead polymer, the total capacity of the aminomethylated bead polymer, the basicity yield and the results of the stability tests for the polymers obtained in Example 2 and in Comparative Example 2.alpha. are summarized.

DEPR:

The reaction is carried out as described in Example 1 except that 131.15 g of polymer C (particle size: 0.3-0.8 mm) were now used instead of polymer A used in Example 1. Yield of amidomethylated resin: 690 ml.

DEPR:

The 690 ml of amidomethylated bead polymer were saponified in 1380 ml of 27% strength by weight of sodium hydroxide solution under the conditions described in Example 1. Yield of aminomethylated bead polymer: 490 ml.

DEPR:

In the Table following the Examples, the yields of amidomethylated and aminomethylated bead polymers, the total capacities of the aminomethylated bead polymers, the basicity yields and the results of the stability tests for the polymers obtained in Example 3 and in Comparative Example 3.alpha. are summarized.

CLPR:

1. In the process for the preparation of anion exchangers based on crosslinked,

water-insoluble organic polymers containing aromatic nuclei, which process comprises (a) producing N-hydroxymethylphthalimide by reaction of phthalimide with aqueous formaldehyde solution in swelling agents in the presence of bases, (b) directly amidomethylating said polymers with N-hydroxymethylphthalimide prepared according to (a) in the presence of Friedel-Crafts catalysts and swelling agents and (c) finally saponifying the amidomethylated polymers to form the aminomethylated polymers, the improvement which comprises using in the first reaction step (a), as the base for producing N-hydroxymethylphthalimide a sodium hydroxide solution and adding this sodium hydroxide solution in such an amount and at such a rate that in the reaction mixture a pH-value is maintained in the range of 5 to 6, wherein the process improves the stability of the polymer.

CLPR:

3. The process of claim 1, wherein an acetic acid ester of N-hydroxymethylphthalimide is the amidomethylating agent and sulphonic acid is the Friedel-Craft catalyst.

CLPR:

5. A process according to claim 1, which further comprises directly converting the N-hydroxymethylphthalimide from (a) to a bis(phthalimidomethyl) ether and directly amidomethylating said polymers with the bis(phthalimidomethyl) ether.

CLPR:

6. A process according to claim 1, which further comprises directly converting the N-hydroxymethylphthalimide from (a) to an ester of N-hydroxymethylphthalimide and directly amidomethylating said polymers with the ester of N-hydroxymethylphthalimide.

CLPR:

7. A process according to claim 5, wherein bis(phthalimidomethyl) ether is the amidomethylating agent and sulphuric trioxide is the Friedel-Craft catalyst.

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L5: Entry 5 of 5

File: USPT

Nov 30, 1976

DOCUMENT-IDENTIFIER: US 3994719 A

TITLE: Resins for separating heavy metals consisting of thiourea-group-containing macroporous vinyl aromatic crosslinked matrixes

BSPR:

Unless the macroporous base polymer already contains primary and/or secondary amino groups resulting from the use of corresponding aromatic monovinyl compounds e.g. of p-vinyl-benzylamine, primary and/or secondary amino groups are introduced into the base polymer by methods known per se. The introduction of these amino groups into the base polymer is known; reference is made, for example, to the introduction of groups of this kind by chlormethylation and subsequent amination (U.S. Pat. No. 2,629,710), or by chlormethylation and subsequent reaction with potassium phthalimide (British Patent No. 767,821), or by amidomethylation and subsequent hydrolysis (British Patent No. 867,449 (= U.S. Pat. No. 3,006,866)). In addition, the introduction of groups of the kind in question is described in German Patent No. 1,045,102.

BSPR:

The synthetic resins according to the invention are used for adsorbing metal compounds in the manner normally adopted for ion exchangers, for example by filling a column with the synthetic resins according to the invention and charging the column thus filled with the solution to be worked up. The column can be charged either from beneath or from above. Similarly, the filter bed can be in the form of a fixed bed or in the form of a fluidized bed. The synthetic resins according to the invention are particularly suitable for adsorbing silver, mercury and gold compounds, and for adsorbing compounds of the platinum metals such as palladium, platinum, iridium and rhodium. The solutions to be worked up can contain these ions either individually or in admixture. The concentration of the metal compounds in the solutions to be worked up is by no means critical and can fluctuate within wide limits. The same applies as regards the pH value of the solutions to be worked up.

BSPR:

The invention is illustrated in the following Examples. In the following Examples there are used for the preparation for the resins of the present invention as vinylaromatic base polymer containing primary and/or secondary amino groups weakly basic anion exchangers. These anion exchangers were obtained by introducing primary and/or secondary amino groups into macroporous, crosslinked vinylaromatic base polymer of known porosity, surface and crosslinking. For crosslinking there was used technical grade divinylbenzene (60% divinylbenzene, 40% ethylbenzene).

DEPR:

1000 ml of a macroporous, weakly basic anion exchanger containing primary amino groups (HCl binding capacity 2.75 val) (val = gram equivalent) prepared in accordance with British Patent No. 867,449 (= U.S. Pat. No. 3,006,866) by aminomethylating a styrene bead polymer crosslinked with 5% of divinylbenzene and made porous by addition of 65% by weight (based on the monomer mixture) of a C.sub.12 -hydrocarbon mixture (porosity: 47% by volume; surface: 65 m.sup.2 /g), were washed in a filter tube, first with water and then with ethanol (technically absolute) until the effluent contained only 0.3% of water. 1635 ml of anion exchanger resin swollen in ethanol were isolated.

DEPR:

600 ml of the anion exchanger thus pretreated were suspended in 500 ml of

ethanol, and heated for 8 hours to 80.degree.C following the addition of 109 g of allyl isothiocyanate (1.1 mol). The reaction product was washed with ethanol and with fully desalted water.

DEPR:

200 ml of macroporous, weakly basic anion exchanger swollen in ethanol, as used in Example 1, were reacted with 67.5 g of phenyl isothiocyanate instead of allyl isothiocyanate (0.5 mol) at 50.degree.C, and were further processed in the same way as described in Example 1.

DEPR:

1000 ml of a macroporous weakly basic anion exchanger containing primary amino groups (HCl binding capacity 2.4 val), produced in accordance with British Patent No. 867,449 (= U.S. Pat. No. 3,006,866) by aminomethylating a styrene bead polymer crosslinked with 8% of divinylbenzene and made porous by the addition of 60% (based on the monomer mixture) of a C.sub.12 -hydrocarbon mixture (porosity: 44% by volume; surface:110 m.sup.2 /g), were suspended in 500 ml of fully desalted water, stirred for 16 hours at 30.degree.C following the addition of 105 g of methyl isothiocyanate (1.44 mol) and the product was worked up in the same way as described in Example 1.

DEPR:

1000 ml of the macroporous weakly basic anion exchanger used in Example 3 were reacted with 35 g of methyl isothiocyanate (0.48 mol) and the reaction product was further processed in the same way as described in Example 3.

DEPR:

625 ml of a macroporous weakly basic anion exchanger containing primary amino groups (HCl binding capacity 1.62 val), produced in accordance with German Patent No. 1,054,715 by aminomethylating a styrene bead polymer crosslinked with 5% of divinylbenzene and made porous by the addition of 65% by weight (based on the monomer mixture) of a C.sub.12 -hydrocarbon mixture, were charged to equilibrium with approximately 1 N thiocyanic acid in a filter tube. After the excess acid had been washed out with water, 1000 ml of the anion exchanger thus charged were isolated in the thiocyanate form, suspended in 500 ml of fully desalted water and heated for 7 hours to 180.degree.C in an autoclave. After cooling, the reaction product obtained was washed in a filter tube with fully desalted water, 2% sodium hydroxide (until the effluent was substantially free from thiocyanate ions) and again with fully desalted water (until the effluent was neutral).

DEPR:

300 ml of the macroporous anion exchanger used in Example 5 (HCl binding capacity 0.78 val) were suspended in 450 ml of fully desalted water and converted into the HCl form by the addition of 0.78 val of hydrochloric acid. After 30 minutes, 118.5 g of ammonium thiocyanate (1.56 mol) were added, and the suspension was heated for 8 hours to 140.degree.C in an autoclave. The reaction product was treated in the same way as described in Example 5.

DEPR:

300 ml of the macroporous anion exchanger used in Example 5 (CHl binding capacity 0.78 val) were suspended in 450 ml of fully desalted water. After 30 minutes, 118.5 g of ammonium thiocyanate (1.56 mol) were added and the suspension was heated for 8 hours to 140.degree.C in an autoclave. After cooling, the reaction product was treated in the same way as described in Example 5.

DEPR:

300 ml of the macroporous anion exchanger used in Example 5 (HCl binding capacity 0.78 val) were suspended in 450 ml of fully desalted water and converted into the HCl form by the addition of 0.78 val of hydrochloric acid. After 30 minutes, 1.56 mol of potassium thiocyanate were added and the suspension was heated for 16 hours to 140.degree.C in an autoclave. The reaction product obtained was treated in the same way as described in Example 5.

DEPR:

The macroporous styrene bead polymer used in Example 5 for producing the anion exchanger resin was converted in accordance with German Offenlegungsschrift No. 2,215,956 into a weakly basic anion exchanger resin of the poly-(aminomethyl)-styrene type, resulting in a resin containing approximately 1.5 aminomethyl groups per aromatic nucleus.

DEPR:

290 ml of the anion exchanger resin thus obtained (HCl binding capacity 0.9 val) were suspended in 500 ml of fully desalted water and were converted into the HCl form by the addition of 0.9 val of hydrochloric acid. After 30 minutes, 137 g of ammonium thiocyanate were added, the reaction mixture was heated for 16 hours to 140.degree.C and was subsequently worked up in the same way as described in Example 5.

DEPR:

1000 ml of the macroporous weakly basic anion exchanger used in Example 5 were washed in a filter tube with ethanol (technical and absolute) until the eluate had a water content of 0.4%. 300 ml of the anion exchanger thus pretreated, with an acid-binding capacity of 0.5 val, were suspended in 500 ml of ethanol and, following the introduction of 24.5 g of sulphuric acid (100%) and 76 g of ammonium thiocyanate, were stirred for 8 hours at 140.degree.C in an autoclave. The reaction product was further processed in the same way as described in Example 5.

DEPR:

300 ml of the anion exchanger swollen in ethanol, as described in Example 10, were washed with toluene in a filter tube until the effluent was substantially free from ethanol. The exchanger was then suspended in 400 ml of toluene and, following the addition of 25.0 g of sulphuric acid (100%) and 76 g of ammonium thiocyanate, was heated for 8 hours to 140.degree.C in an autoclave. After cooling, the reaction product was washed with ethanol and then worked up in the same way as described in Example 5.

DEPR:

150 ml of the macroporous anion exchanger resin used in Example 5 (HCl binding capacity 0.4 val) were suspended in 200 ml of fully desalted water and converted into the HCl form with 0.4 val of hydrochloric acid. After 30 minutes, 45.5 g of ammonium thiocyanate and 66.5 g of benzyl ammonium thiocyanate were added, and the suspension was heated for 16 hours to 140.degree.C in an autoclave. After cooling, the reaction product was washed with 1 litre of ethanol in a filter tube and then worked up in the same way as described in Example 5.

DEPR:

150 ml of the resulting macroporous anion exchanger resin of the poly-(aminostyrene)-type with an HCl binding capacity of 0.22 val were stirred for 30 minutes in 220 ml of 1 N hydrochloric acid and heated for 8 hours to 120.degree.C in an autoclave following the addition of 40 g of ammonium thiocyanate. The reaction product was further processed in the same way as described in Example 5.

DEPR:

63 ml of a macroporous weakly basic anion exchanger with secondary amino groups (HCl binding capacity 0.125 val), produced in accordance with German Patent No. 1,495,762 by amidomethylating (with N-chloromethyl-N-methylacetamide) and subsequently hydrolysing a bead-form styrene polymer crosslinked with 4% of divinylbenzene and made porous by the addition of 60%, based on the monomer mixture, of a C.sub.12 -hydrocarbon mixture (porosity: 44% by volume; surface 45. m.sup.2 /g), were suspended in 150 ml of fully desalted water, after which the pH value of the suspension was adjusted to around 0.5 by the addition of 0.25 val of hydrochloric acid. After 60 minutes, 19 g of ammonium thiocyanate (0.25 mol) were added and the suspensions was heated for 16 hours to 160.degree.C. The reaction product was isolated and worked up in the same way as described in Example 5.

DEPR:

1000 ml of the macroporous anion exchanger used in Example 5 were charged to equilibrium with 3% hydrochloric acid in a filter tube. After the excess acid had been washed out with water, 1730 ml of the anion exchanger charged with hydrochloric acid were isolated.

DEPR:

300 ml of the macroporous anion exchanger resin charged with hydrochloric acid (anion-exchange capacity 0.45 val) were suspended in 500 ml of fully desalted water, and heated for 8 hours to 180.degree.C in an autoclave following the addition of 103 g of thiourea (1.35 mol). The reaction product was worked up in

the same way as described in Example 5.

DEPR:

1000 ml of the macroporous weakly basic anion exchanger used in Example 5 with an HCl binding capacity of 2.6 val were suspended in 1000 ml of fully desalted water, and heated for 8 hours to 150.degree. - 155.degree.C in an autoclave following the addition of 600 g of thiourea (7.9 mols). After cooling, the reaction product obtained was washed in a filter tube successively with fully desalted water, 2% sodium hydroxide solution and again with fully desalted water (until the effluent was neutral).

DEPR:

1000 ml of the macroporous, weakly basic anion exchanger resin with primary amino groups used in Example 3 (HCl binding capacity 2.4 val) were heated for 40 hours to reflux temperature (110.degree.C) in aqueous suspension together with 1630 g of thiourea. The pH value of the suspension was maintained at 4 - 7 by the addition in portions of a total of 2.1 val of hydrochloric acid. The reaction solution was then run-off while still warm and the reaction product was isolated and worked up in the same way as described in Example 5.

DEPR:

Approximately 1.35 aminomethyl groups per aromatic nucleus were introduced in known manner in accordance with DOS No. 2,215,956 into a styrene bead polymer crosslinked with 7% of divinylbenzene and made porous by the addition of 65% by weight, based on the monomer mixture, of a C.sub.12 -hydrocarbon mixture (porosity: 47% by volume; surface: 95 m.sup.2 /g). 200 ml of the anion exchanger resin thus obtained (HCl binding capacity 0.48 val) were suspended in 500 ml of fully desalted water, converted into the HCl form by the addition of 0.48 val of hydrochloric acid and heated for 16 hours at 160.degree.C following the addition of 73 g of thiourea. The reaction product was worked up in the same way as described in Example 5.

DEPR:

200 ml of the macroporous anion exchanger resin used in Example 5 (HCl binding capacity 0.52 val) were suspended in 400 ml of fully desalted water and converted into the HCl form by the addition of 0.52 val of hydrochloric acid. 140 g of methyl thiourea (1.56 mol) were then added, after which the suspension was heated for 8 hours to 180.degree.C in an autoclave. After cooling, the reaction product was washed in a filter tube successively with ethanol, 2% sodium hydroxide solution and fully desalted water (until the effluent was neutral).

DEPR:

200 ml of the macroporous anion exchanger used in Example 5 were converted into the HCl form in the same way as described in Example 19. Following the addition of 158 g of phenyl thiourea (1.04 mol), the suspension was heated for 8 hours to 160.degree.C in an autoclave and was subsequently worked up in the same way as described in Example 19.

DEPR:

1000 ml of the macroporous, weakly basic anion exchanger resin with primary amino groups used in Example 3 (HCl binding capacity 2.4 val) were washed with ethanol (technical and absolute) in a filter tube until the effluent contained only 0.2% of water. 1330 ml of the anion exchanger swollen in ethanol were then isolated.